Chiral Lithiated Phosphoric Triamides: Structure, Reactivity, and Salt Effects

by **Jürgen F.K. Müller**[1])* and **Margareta Zehnder**

University of Basel, Institute of Inorganic Chemistry, Spitalstrasse 51, CH-4056 Basel

and **Frédérique Barbosa**

University of Basel, Institute of Organic Chemistry, St. Johanns-Ring 19, CH-4056 Basel

and **Bernhard Spingler**

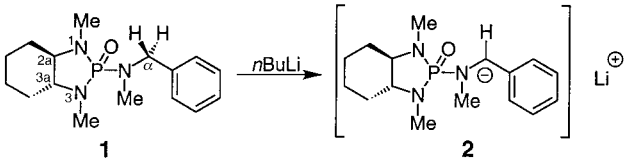
Massachusetts Institute of Technology, Department of Chemistry, Cambridge, Massachusetts, 02139, USA

The theoretical structure of a cyclic phosphoric triamide **3** and of its monolithiated isomers **4**–**6** was calculated by *ab initio* methods (*Fig. 1*, *Tables 1* and *2*). The global minimum in **4** consists of a five-membered Li–C–N–P–O chelate. The intermediates **5** and **6** are, relative to **4**, energetically unfavorable by 15 and 18 kcal mol^{-1}, respectively, due to distortion in order to accommodate the N-complexation of the Li^+ ions. NMR Investigations (^{1}H, ^{13}C, ^{31}P, and ^{7}Li) of the lithiated bicyclic phosphoric triamide **1** were performed (*Tables 3–5*). The lithium aminomethanide **2** is characterized by a sp^3-hybridized anion supporting Li–C contacts. The anions exist in a monomer-dimer equilibrium in solution (*Scheme 2*). Trapping reactions of *rac*-**2** with carbonyl compounds generated the corresponding amino-alcohol derivatives with high diastereoselectivities (*Scheme 3*, *Table 6*). A rational for the stereochemical outcome is given (*Fig. 4*). In the presence of LiBr, a P–N bond cleavage occurred on reaction of *rac*-**2** with aldehydes, which allowed the synthesis of (1-hydroxylalkyl)phosphonic diamides (*Scheme 5*, *Table 7*).

1. Introduction. – Chiral representatives of phosphoric triamides have rarely been considered as reagents in asymmetric synthesis [1]. This attitude, which is presumably influenced by the well-known toxicity of hexamethylphosphoric triamide (HMPA) and its derivatives, started to change only recently [2]. For example, *Denmark* and co-workers successully used chiral phosphoric triamides as catalysts for the asymmetric addition of trichlorosilyl ester enolates to aldehydes [3]. In organolithium chemistry, the related reactivity and selectivity effects of HMPA and its derivatives are usually rationalized in terms of changes in the aggregation state or in ion-pair structure. The breaking up of aggregates to form reactive monomers or solvent-separated ion pairs is often invoked [4]. Our purpose was to use these phosphorus(V) compounds in asymmetric reactions, to take advantage of the strongly donating abilities of Li^+, and to combine these properties with a suitable chiral auxiliary. The *trans*-1,2-diaminocyclohexane motif was selected because it is a very effective chiral building block and easily accessible [5]. Our intention was to deprotonate the activated, chiral HMPA analogue **1** with a strong lithium base, generating the corresponding anion **2** [6] (*Scheme 1*).

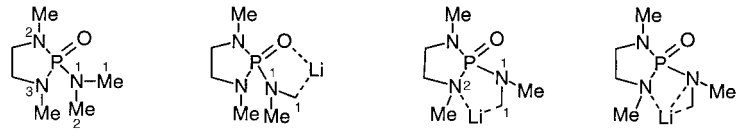
[1]) Tel.: +41-61-2671026; fax: +41-61-2671018; e-mail: muellerju@ubaclu.unibas.ch.

Scheme 1



Electrophilic addition to organolithium compound **2** gave access to a wide range of chiral products [7]. However, the nature of the intermediate in this reaction is unknown. While investigations into the structure of metallated phosphoric triamides are few, there are several structures of organic lithium salts where HMPA functions as a coordinating ligand [8]. The fascinating chemical properties, together with the novel incorporation of a chiral moiety, were the starting point for our investigation of the structure of the lithiated intermediate **2**. Quantum-chemical calculations on related model systems were carried out to locate suitable energy-minima structures [9]. The variety of observable nuclei in NMR spectroscopy (^{1}H, $^{6/7}Li$, ^{13}C, ^{31}P) allowed the investigation of the solution structure of the lithiated intermediate **2** [10]. The reactivity of **2** towards electrophiles, which can precoordinate to this aminomethanide intermediate, was examined and compared with previously reported electrophilic addition reactions with simple alkyl halides. During these studies, we found a remarkable new salt effect in the reaction of lithiated phosphoric triamides with aldehydes in presence of LiBr [11]. This exploration led to the asymmetric synthesis of (1-hydroxyalkyl)-phosphonic diamides, instead of the expected hydroxyalkylation products, where derivatization adjacent to the N-atom should occur. (1-Hydroxyalkyl)phosphonic diamides are easily converted to 1-hydroxyalkylphosphonates which have been shown to possess significant biological activity [12].

Results and Discussion. – 2.1. *Theoretical Structures. Ab initio* calculations of the lithiated model system **3** yielded three different major structural minima **4**–**6** (see *Fig. 1* and *Tables 1* and *2*).



3 **4** **5** **6**

arbitrary numberings

Of these, **4** possesses a Li–C–N–P–O five-membered chelate ring with Li–O complexation and a Li–C contact in an orientation reminiscent of lithiated amides [9][13]. Previous calculations on related lithiated phosphine oxides show the same characteristic features (C,O-complexation) with four-membered ring chelates [14]. Unexpectedly, in **5** no Li–O contact occurs. There, one endocyclic N-atom coordinates to the Li^{+} ion to form a Li–N–P–N–C chelate. Structure **6** differs in having three coordination partners for Li^{+}: the anionic C-atom, the exocyclic N-atom, and one endocyclic N-atom. The Li–O chelate **4** is the structure that has the lowest energy. The

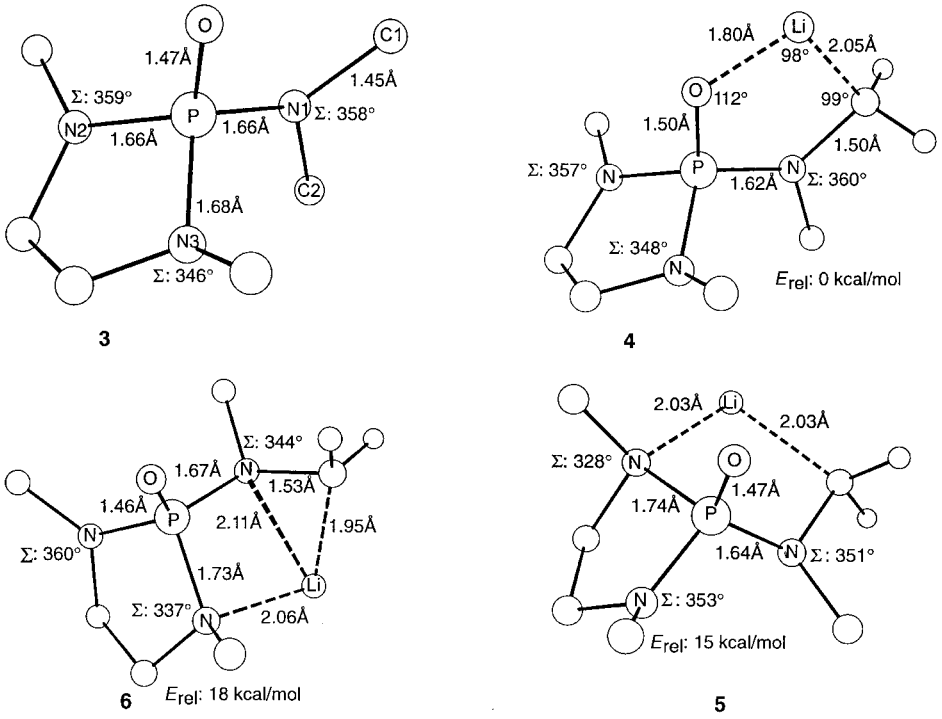


Fig. 1. *Gas-phase structures of the model system* **3** *and the lithium anions* **4**–**6**. Arbitrary numbering.

Table 1. *Bond Lengths* [Å] *and Angles* [°] *of* **3** *and* **4** [a])

	3	**4**		**3**	**4**
P–O	1.47	1.50	O–P–N(1)	109.2	109.5
P–N(1)	1.66	1.62	O–P–N(2)	118.2	114.7
P–N(2)	1.66	1.67	O–P–N(3)	117.2	114.3
P–N(3)	1.68	1.66	P–N(1)–C(1)	121.5	121.5
N(1)–C(1)	1.45	1.50	P–N(1)–C(2)	121.3	120.5
Li–O		1.80	N(1)–C(1)–Li		98.7
Li–C(1)		2.05	C(1)–Li–O		98.1

[a]) The geometries were determined with HF/6-31 + G**. Arbitrary numbering.

Li–N chelate **5** and the threefold coordinated lithium salt **6** are significantly energetically unfavorable by 15 and 18 kcal mol^{-1}, respectively, relative to **4**. Lithiation of the phosphoric triamide **3** causes a number of distinctive structural changes in **4**–**6**: in **4**, an increase in the P–O bond length (1.50 *vs.* 1.47 Å) is observed, which is not the case for the other isomers. The N(1)–C(1) bond in **4** is longer (1.50 *vs.* 1.45 Å), while the P–N(1) bond of the chelate ring is shorter (1.62 *vs.* 1.66 Å) (arbitrary numbering). The P–N(2) bond of the chelate N-atom in **5** is longer (1.74 *vs.* 1.66 Å), as is the N(1)–C(1) bond of the chelate ring (1.50 *vs.* 1.45 Å). The Li–C(1) contact results in a small shortening of the P–N(1) bond in **5** (1.64 Å). For **6**, a significant increase in bond

Table 2. *Bond Length* [Å] *and Angles* [°] *of* **5** *and* **6** [a])

	5	**6**		**5**	**6**
P–O	1.47	1.46	O–P–N(1)	120.6	117.4
P–N(1)	1.64	1.67	O–P–N(2)	113.3	114.9
P–N(2)	1.74	1.66	O–P–N(3)	114.2	116.8
P–N(3)	1.67	1.73	P–N(1)–C(1)	115.9	115.6
N(1)–C(1)	1.50	1.53	P–N(1)–C(2)	118.3	113.1
Li–C(2)	2.02	1.95	N(1)–C(2)–Li		73.5
N(1(–Li		2.11	N(1(–C(1(–Li	99.8	101.3
N(2)–Li	2.03	2.06	C(2)–Li–N(1)		43.9

[a]) The geometries were determined with HF/6-31 + G**. Arbitrary numbering.

length occurs for the N(1)–C(1) bond (1.53 *vs.* 1.45 Å). This contraction is less pronounced for both P–N bonds of the Li–C–N–P–N ring (1.67 *vs.* 1.66 Å and 1.73 *vs.* 1.68 Å). The key finding is that **4** has both Li–O and Li–C(1) bonds, so that the C(1) atom is sp^3 and pyramidal. The anionic center in all three isomers tends towards a pyramidal geometry as demonstrated by the sum of angles around the anionic C-atoms. The N–Li contacts in **5** and **6** induce a significant deformation of the five-membered ring geometry. This leads to a higher degree of pyramidalization of the coordinating N-atom as indicated by its sum of angles (328° and 353° in **5**, 337° and 360° in **6** compared to 348 and 357° in **4**). This effect is the origin of the higher energies of the isomers **5** and **6**. Even the threefold coordination of the Li^+ ion in **6** is not able to compensate for this. In summary, our model calculations favor strongly isomer **4**, which contains most likely the relevant structural motif of intermediate **2**. The question arises as to whether there is any 'dipole stabilization', which means that a shortening of the P–N and elongation of the P–O bonds should occur [15]. Indeed, the P–O distance became 0.032 Å longer and the P–N bond 0.036 Å shorter. But these changes are too marginal for a 'dipole-stabilized' anion, where a P–N double-bond character is expected.

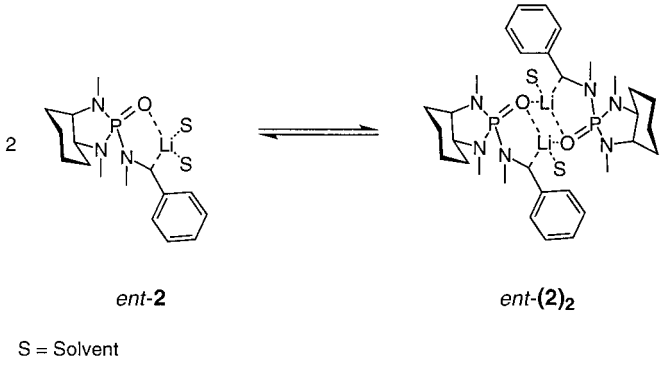
2.2. *Solution Structures.* A full set of NMR spectra of *ent*-**1** and its lithiated counterpart *ent*-**2** (^{1}H, ^{7}Li, ^{13}C, ^{31}P) were recorded in (D_8)THF at variable temperatures to determine which structural changes occur upon lithiation. Examination of *ent*-**1** and *ent*-**2** by ^{13}C-NMR spectroscopy at 25° revealed significant changes in chemical shifts on lithiation. The most dramatic effect was observed for the C(α)-atom (see *Scheme 1*) which was shifted by 12.8 ppm downfield (see *Table 3*). In addition, the ring MeN groups showed an upfield shift of *ca.* 14 ppm. Smaller changes were seen for the aromatic C-atoms, with C_{ipso} shifted downfield by 5.4 ppm, while C_o, C_m, and C_p were slightly shifted upfield ($\Delta\delta = 0.7$, 0.4 and 0.3 ppm, resp.) Interestingly, only one of the

Table 3. *^{13}C-NMR Data of* ent-**1** *and* ent-**2** [a])

	C(α)	C_o	C_m	C_p	C_{ipso}	MeN (exocyclic)	C(3a)/C(7a)
ent-**1**	53.8	128.8	129.2	127.6	140.6	32.9	64.5, 65.8
ent-**2**	66.6	128.1	128.8	127.3	146.0	34.9	64.4, 71.5

[a]) In (D_8)THF at 25°; δ in ppm.

*Scheme 2. Schematic Presentation of the Monomer-Dimer Equilibrium of ent-***2**



bridgehead C-atoms C(3a) and C(7a) underwent a strong downfield shift ($\Delta\delta =$ 5.7 ppm). It is reasonable to assume that a homochiral dimer *ent*-(**2**)$_2$ is forming, in which one bridgehead C-atom comes into close proximity to the anisotropic field of the phenyl ring of the second coordinated lithiated phosphoric-triamide moiety (*Scheme 2*).

This interpretation is also supported by NOE investigations which showed interactions between one ring MeN group and the H_o of the aromatic ring. Several solid-state structures for the related lithiated phosphine oxides are known, most of them as dimers [16]. In solution, monomer-dimer equilibria have been established [17]. Further investigations were performed at low temperatures to slow down inter- and intra-aggregate exchange processes. At $-108°$, no significant changes were noted in the ^{13}C-NMR spectrum of *ent*-**2**, except for a general line broadening which can be attributed to the increasing viscosity rather than to coalescence phenomena. A remarkable C,H coupling constant ^1J(C,H) = 129 Hz was found, indicating a significant degree of pyramidalization at C(α), which would suggest that a Li–C contact should be present, but a ^{13}C,^{7}Li coupling constant at $-108°$ was not resolved. Minor differences from *ent*-**1** were observed in the ^{1}H-NMR spectrum of *ent*-**2** at 25° (*Table 4*). All phenyl protons were shifted upfield to a small extent ($\Delta\delta \leq 0.4$ ppm). Reexamination of the anion at $-108°$ revealed no significant changes. The ^{31}P-NMR data of *ent*-**2** at 25° compared to those of *ent*-**1** (*Table 5*) showed two ^{31}P resonances in a 1 : 1 ratio shifted slightly downfield ($\Delta\delta = 0.9$ and $\Delta\delta = 3.4$ ppm). A reasonable interpretation of these data is again that there exist a monomer-dimer equilibrium between *ent*-**2** and *ent*-(**2**)$_2$ (see *Scheme 2*). After cooling to $-108°$ a new ^{31}P resonance appeared at 4.4 ppm, which led to a 5 : 20 : 1 ratio of the observed signals. Obviously, at $-108°$, an additional oligomer species of *ent*-**2** exists in equilibrium. Remarkably, at $-108°$ no ^{7}Li,^{31}P coupling was observed. The ^{7}Li-NMR spectrum of *ent*-**2** at 25° displayed a broad *s* at -0.22 ppm, which shifted to -0.51 pm at $-108°$ (see *Table 5*). Taken together, these data imply the presence of a equilibrating mixture of monomers and dimers. We conclude that, according to the ^1J(C,H) coupling constant of 129 Hz, the lithiated C(α)-atom adopts an sp^3 hybridization, supporting a Li–C contact as calculated for in the gas phase.

Table 4. *^{1}H-NMR Data of* ent-**1** *and* ent-**2** [a])

	MeN (exocyclic)	H_o	H_m	H_p	MeN (ring)	H–C(3a), H–C(7a)
ent-**1**	4.17	7.17	7.2–7.4	7.2–7.4	2.43	2.47–2.7
ent-**2**	2.15	7.0–7.4	7.0–7.4	7.0–7.4	2.35–2.7	2.35–2.70

[a]) In (D_8)THF at 25°; δ in ppm.

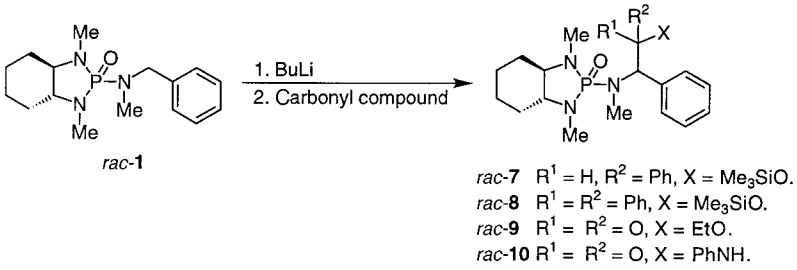
Table 5. *^{31}P- and ^{7}Li-NMR Data of* ent-**1** *and* ent-**2** [a])

	^{7}Li (25°)	^{7}Li (– 108°)	^{31}P (25°)	^{31}P (– 108°)
ent-**1**	–	–	30.7	–
ent-**2**	– 0.22	– 0.51	31.6, 34.1	4.4, 31.7, 33.9

[a]) In (D_8)THF; δ in ppm.

2.3. *Reaction of Lithiated Phosphoric Triamides with Electrophiles.* Hydroxyalkylation of *rac*-**2**, which was prepared by treatment of *rac*-**1** with BuLi at – 78° in THF, was achieved by addition of PhCHO in presence of trimethylsilyl chloride (Me_3SiCl) and yielded the silylated alcohol derivatives *rac*-**7** in 24% yield and a diastereoisomer ratio of 68 : 21 : 11 (see *Scheme 3* and *Table 6*). An X-ray structure of the main diastereoisomer of *rac*-**7** is shown in *Fig. 2*.

Scheme 3



rac-**1**

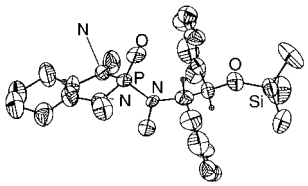
rac-**7** R^1 = H, R^2 = Ph, X = Me_3SiO.
rac-**8** R^1 = R^2 = Ph, X = Me_3SiO.
rac-**9** R^1 = R^2 = O, X = EtO.
rac-**10** R^1 = R^2 = O, X = PhNH.

Treatment of *rac*-**2** with benzophenone/Me_3SiCl gave a mixture of silylated *rac*-**8** (35%) in a like/unlike (lk/ul) ratio of 86 : 14 [18] (*Scheme 3*, *Table 6*). Addition of *rac*-**2** to a CO_2 equivalent, *i.e.*, ethyl chloroformate (ethyl carbonochloridate), gave the phenylglycine derivative *rac*-**9** in 25% yield in a ratio of 87 : 13. The reaction of *rac*-**2** with phenyl isocyanate proceeded with a much better yield (94%), but with a slightly

Table 6. *Trapping of rac*-**2** *with Carbonyl Compounds*

	R^1	R^2	X	D.r.[a])	Yield [%]
rac-**7**	Ph	H	Me_3SiO	68 : 21 : 11	24
rac-**8**	Ph	Ph	Me_sSiO	86 : 14	35
rac-**9**	O	O	EtO	87 : 13	25
rac-**10**	O	O	PhNH	80 : 20	94

[a]) Diastereoisomer ratio.

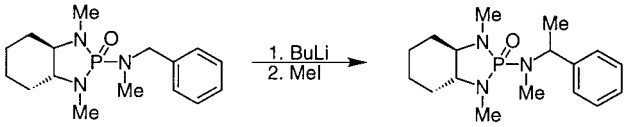


rac-**7**

Fig. 2. *Molecular structure of* rac-**7**. H-Atoms, except those at the stereogenic centers and the O-atoms, are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

lower selectivity (80:20) to give *rac*-**10**. Comparison with the previously reported product ratios obtained by trapping reactions of *rac*-**2** with simple alkyl halides revealed similar selectivities. In the case of the reaction of *rac*-**2** with MeI, an 81:19 ratio of lk/ul diastereoisomers *rac*-**11** was obtained (*Scheme 4*). Such equivalent diastereoselectivities were also achieved in the reactions with i-PrI, BzBr, and allyl bromide as electrophiles under identical conditions.

Scheme 4



rac-**1** *rac*-**11**

A previously reported salt effect, observed when achiral phosphoric triamides were alkylated in the presence of LiBr, prompted us to run hydroxyalkylations of *rac*-**2** in the presence of 4 equiv. of LiBr [6][11]. Surprisingly, the alkylation products formed from *rac*-**2** were different from the product type reported [6][11]; instead of the exclusive reaction of an aminomethanide equivalent with PhCHO, the (1-hydroxyalkyl)phosphonic diamide *rac*-**12** was obtained in moderate yield (52%) with low diastereoselectivity (55:45) as a single product (see *Scheme 5* and *Table 7*). This unexpected result, together with the well-known biological activity of (1-hydroxyalkyl)phosphonic acid derivatives, encouraged us to continue our investigations [19]. Thus, electronic modification of the aromatic aldehydes used had only a marginal influence on the observed diastereoisomer ratios of the products *rac*-**13** and *rac*-**14** (*Table 7*); however, the yields increased slightly in the presence of electron-withdrawing groups (51% of *rac*-**14**). Chelating substituents in the *ortho*-position of the aldehyde, *e.g.*, as in salicylaldehyde, led to higher diastereoisomer ratios (62:38) and good yields (55% of *rac*-**15**). The diastereoselectivity of hydroxyalkylation was highest in *rac*-**16** (77:23) during the reaction of *rac*-**2** with the sterically demanding pivalaldehyde. The structure of the major diastereoisomer of *rac*-**16** was established by X-ray analysis (see Fig. 3).

2.4. *Origin of the Diastereoselectivity.* At present, we have to consider at least two possibilities which control the stereochemical course of the alkylation reaction. For a configurationally labile anion, the step that determines the configuration is derived from the rate of the electrophilic attack at **2** [20]. In this case, the reactivity of the electrophile should have a crucial influence on the obtained diastereoselectivity. In contrast, for a configurationally stable anion, the deprotonation step becomes the

Scheme 5

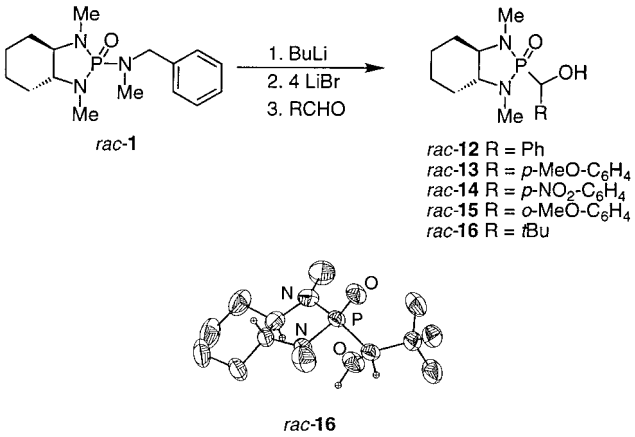


Fig. 3. *Molecular structure of* rac-**16**. H-Atoms, except those at the stereogenic centers and the O-atoms, are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

Table 7. *Reaction of* rac-**2** *with Aldehydes in the Presence of 4 equiv. of LiBr*

	R	D.r.[a])	Yield [%]
rac-**12**	C_6H_5	55 : 45 (82 : 19 [b])	52
rac-**13**	*p*-MeO-C_6H_4	53 : 47 (96 : 4 [b])	32
rac-**14**	*p*-NO_2-C_6H_4	54 : 46	51
rac-**15**	*o*-MeO-C_6H_4	62 : 38	55
rac-**16**	*t*-Bu	77 : 23 (80 : 20 [b])	32

[a]) D.r. = diastereoisomer ratio. [b]) After recrystallization from hexane.

stereochemistry-controlling factor [21]. As a working hypothesis, we suggest an electrophilic attack on the configurationally stable monomeric intermediate **2** as a simple model for the origin of diastereoselectivity (see *Fig. 4*). The methyl group at the exocyclic N-atom of **2** and the phenyl ring prevent an attack on the electrophile RX from the lower side of the molecule. Therefore, the electrophile has to approach from the upper part, where complexation of the axial O-atom may also take place. The upwardly oriented Me group at the ring N-atom prevents attack from the *unlike* side. This explains the selectivities observed in the addition reaction with simple alkyl halides and carbonyl compounds (*Schemes 3* and *4*, *Table 6*).

Explaining the observed salt effect is less straightforward. Interestingly, after aqueous workup, benzaldehyde was always found in the hydroxyalkylation reaction mixture. One explanation for the latter is the formation of a benzenemethanimine intermediate, which occurs after addition of LiBr to the anion **2**. As a consequence, a phosphoric diamide anion that reacts with the free aldehyde RX (X = CHO) must be generated to give the observed α-hydroxyphosphonic diamides (*Scheme 5*, *Table 7*). Indeed, it is known from the reaction of metallated chiral phosphoric diamides with aldehydes that such intermediates react with a comparable selectivity [22]. However, it is still not clear if the free anion **17** is formed, or if a highly activated LiBr complex **18** with similar reactivity is present.

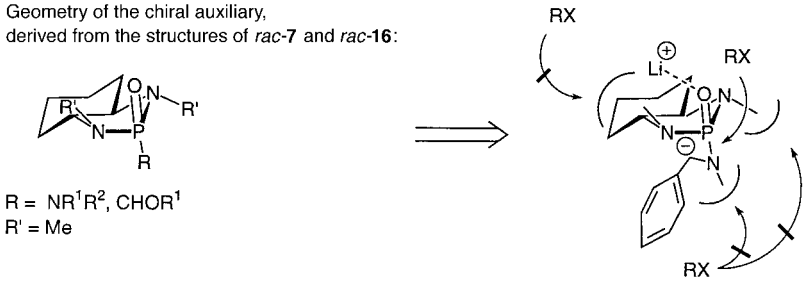
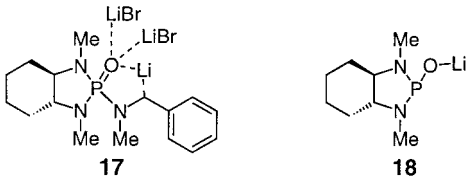


Fig. 4. *A model for the electrophilic attack on* **2**. The geometry of the chiral motif is derived from the X-ray structures of *rac*-**7** and *rac*-**16** (see also *Figs. 2* and *3*)[2])



Conclusion. – According to quantum-chemical calculations, lithiated phosphoric triamides with three different energy-minima structures could be identified in the gas phase, with **4** as the distinctly most stable one. NMR Investigations of the solution structure of lithiated *N*-benzylphosphoric triamide *ent*-**2** gave evidence for a Li–C contact. Various temperature-dependent aggregates exist. Trapping experiments with alkyl halides or activated carbonyl compounds led to the related products in good yields and high diastereoselectivity. A rationalization of the stereochemical course of these reactions was possible with the underlying assumption that *i*) monomeric species are present which are more reactive as aggregates, *ii*) the aminomethanide anion **2** is configurationally stable during the reaction with electrophiles, and *iii*) the electrophilic attack from the *like* side is favored. Addition of 4 equiv. of LiBr had a remarkable effect on the reactivity of **2**. Exclusively (1-hydroxyalkyl)phosphonic diamides were formed in high yields and modest to good diastereoselectivities.

B. S. thanks the *Stipendienfonds der Basler Chemischen Industrie* for a stipend.

Experimental Part

1. *General*. All reactions were carried out in absolute solvents under Ar with syringe and *Schlenk* techniques in oven-dried glassware. THF and Et_2O were distilled under Ar from K/benzophenone and Na/benzophenone, resp. Column chromatography: *Uetikon* silica gel *60*, 60–200 μm; FC = flash chromatography. TLC: *Machery Nagel Alugram® Sil G/UV254* plates. ^{1}H-, ^{13}C-, ^{31}P- and ^{7}Li-NMR Spectra: *Bruker DRX 600*, *Varian VXR 400*, and *Varian Gemini 300*; chemical shifts δ in ppm rel. to $SiMe_4$ (= 0.00 ppm), THF (= 1.73 ppm), $(PhO)_3PO$ in $CDCl_3$ (= – 18 ppm), or LiCl in D_2O (= 0.00 ppm); coupling constants *J* in Hz. Data of minor isomers obtained in mixtures with major isomers are given only when an unequivocal assignment was possible. MS: *VG 70–250*;

---

[2]) Crystallographic data (excluding structure factors) for the structures reported in this publication have been deposited with the *Cambridge Crystallographic Database Center* as deposition no. CCDC 115094 and CCDC 115095. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+ 44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

NBA = 3-nitrobenzyl alcohol, Thio = 1-thioglycerin; EI, 70 eV, in *m/z* (rel. %). Elementary analyses were carried out at the University of Basel, Institute of Organic Chemistry, Microanalytical Laboratory.

2. *Computational Methods.* The *ab initio* calculations presented were performed with the Gaussian94 program suite. All geometries were optimized at the HF level of theory with the basis set 6-31 + G**. To assess the effect of electron correlation, MP2/6-31 + G** single point calculations were made on the HF/6-31 + G** structures [23].

3. *X-Ray Analysis of* rac-**7** *and* rac-**16**. *rac*-**7** crystallizes in the monoclinic space group *C*1*c*1 and *rac*-**16** in the monoclinic space group $P2_1/n$. Unit-cell parameters were determined by carefully centering 25 independent, strong reflections with $19° \leq \Theta \leq 42°$. Data collection was carried out at 293 K with an *Enraf-Nonius-CAD4* diffractometer equipped with a Cu$K\alpha$ fine focus sealed tube (λ 1.54180 Å) for *rac*-**16** and a Mo$K\alpha$ fine focus sealed tube (λ 0.71069 Å) for *rac*-**7**, with a graphite monochromator. For *rac*-**7** and *rac*-**16**, φ-scans were used to determine the absorption. The structures were solved by direct methods using the program SIR92 [24]. Anisotropic least-squares full-matrix refinement was carried out on all non-H-atoms using the program CRYSTALS [25]. The H-atoms bonded to the stereogenic centers and the O-atoms in *rac*-**7** and *rac*-**16** were localized in the difference map and refined restraining the C–H distance to 0.96 Å. All other H-atoms were in calculated positions. *Chebychev* polynomial weights were used to complete the refinement [26]. Scattering factors were taken from the 'International Tables for Crystallography' (Vol. IV, Table 2.2B). Crystal data and other numerical details of the structure determinations are listed in *Table 8*.

General Procedure (GP 1) for Trapping Reactions with Electrophiles. To a soln. of **1** (*ca.* 0.5 mmol) in dry THF (3 ml), BuLi (1.1 equiv.) in hexane was added at −78°. After stirring for 1 h at −78°, a soln. of the electrophile (1 equiv.) in THF (1 ml) was added dropwise. After decolorization of the purple soln., the mixture was treated with sat. $NaHCO_3$ soln. and extracted with AcOEt. The org. layer was dried (Na_2SO_4) and evaporated and the residue purified by FC to afford the diastereoisomeric products. The diastereoisomer ratios were determined by integration of the ^{31}P-NMR spectra of the crude products.

rac-trans-N-*{1,2-Diphenyl-2-[(trimethylsilyl)oxy]ethyl}-octahydro-*N,*1,3-trimethyl-2*H-*1,3,2-benzodiazaphosphol-2-amine 2-Oxide* (*rac*-**7**). With *rac*-**1** (152.0 mg, 0.495 mmol) and a benzaldehyde/Me_3SiCl soln. (each

Table 8. *Experimental Data for the X-Ray Diffraction Studies of* rac-**7** *and* rac-**16**[a])

	rac-**7**	*rac*-**16**
Formula	$C_{26}H_{40}N_3O_2PSi$	$C_{29}H_{36}HN_3O_2P$
space group	*C*1*c*1	$P2_1/n$
a [Å]	14.410(9)	11.254(1)
b [Å]	19.232(3)	21.534(2)
c [Å]	11.859(2)	12.041(2)
α [°]	90	90
β [°]	121.94(6)	113.39(1)
γ [°]	90	90
Volume [Å^3]	2789(1)	2678.4(6)
Z	4	4
Crystal dimensions [mm]	0.39 × 0.42 × 0.45	0.09 × 0.12 × 0.38
Temperature [K]	293	293
Θ_{max}	26.32	77.50
Radiation	MoK_α (λ 0.71079 Å)	CuK_α (λ 1.54178 Å)
Scan mode	$\omega/2\Theta$	$\omega/2\Theta$
μ [μm^{-1}]	0.16	1.12
Max./min. transmission	1/0.42	1/0.84
No. of independent refl.	2545	3707
No. of refl. incl. in refinement	1629 ($F > 3\sigma(F)$)	2400 ($F > 3\sigma(F)$)
No. of parameters	298	333
R (· 100%)	10.54	6.02
R_W (· 100%)	11.82	6.49
$\Delta\rho$ [e Å^{-3}]	0.69/ − 0.66	0.27/ − 0.37

[a]) Weighting scheme, $\omega \cdot (1-(\delta F/6\sigma F)^2)^2$; R value, $R = \Sigma(|F_o| - |F_c|)\Sigma|F_o|$, R_w value, $R_w = \{\Sigma(|F_o| - |F_c|)^2 \cdot \omega)/\Sigma F_o^2 \cdot \omega\}^{1/2}$).

0.678M in THF, 1.08 mmol), according to *GP 1*. FC (AcOEt/EtOH 20:1; R_f 0.29) afforded 57.6 mg (24%) of *rac*-**7**, diastereoisomer ratio 68:21:11. Colorless solid. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: −0.24 (*s*, Me_3Si); 0.85–1.35 (*m*, $CH_2(5)$, $CH_2(6)$); 1.50 (*d*, ^3J(P,H) = 10.3, 1 MeN); 1.6–1.9 (*m*, 2 CH_2); 2.01 (*d*, ^3J(P,H) = 11.8, 1 MeN); 2.34 (*d*, ^3J(P,H) = 10.6, 1 MeN); 2.35–2.5 (*m*, H–C(3a), H–C(7a)); 5.1–5.4 (*m*, NC*H*(C*H*)Ph); 7.2–7.4 (*m*, 6 arom. H); 7.5–7.63 (*m*, 4 arom. H); minor isomer I: −0.23 (*s*, Me_3Si); 1.55 (*d*, ^3J(P,H) = 11.7, 1 MeN); 1.85 (*d*, ^3J(P,H) = 10.6, 1 MeN); 2.31 (*d*, ^3J(P,H) = 11, 1 MeN); minor isomer II: −0.07 (*s*, Me_3Si); 1.57 (*d*, ^3J(P,H) = 10.4, 1 MeN); 2.39 (*d*, ^3J(P,H) = 10.4, 1 MeN); 2.7 (*d*, ^3J(P,H) = 11.8, 1 MeN). ^{13}C-NMR (75 MHz, {^{1}H}, $CDCl_3$): 0.05 (*s*, 3 C, Me_3Si); 24.23 (*s*); 24.28 (*s*); 26.53 (*s*); 26.57 (*s*); 28.18 (*s*); 28.28 (*s*); 28.43 (*s*); 28.49 (*s*); 28.55 (*s*); 28.63 (*s*); 63.14 (*d*); 64.42 (*s*); 65.11 (*d*); 126.18 (*s*, arom. C); 126.90 (*s*, arom. C); 127.52 (*s*, arom. C); 127.60 (*s*, arom. C); 127.62 (*s*, arom. C); 127.67 (*s*, arom. C); 127.69 (*s*, arom. C); 127.72 (*s*, arom. C); 127.79 (*s*, arom. C); 127.84 (*s*, arom. C); 127.86 (*s*, arom. C); 127.96 (*s*, arom. C); 128.02 (*s*, arom. C); 128.16 (*s*, arom. C); 128.33 (*s*, arom. C); 128.43 (*s*, arom. C); 128.48 (*s*, arom. C); 129.39 (*s*, arom. C); 140.27 (*s*, C_{ipso}); 142.9 (*s*, C_{ipso}). ^{31}P-NMR (121 MHz, {^{1}H}, $CDCl_3$): 28.3 (*s*, minor isomer II); 29.6 (*s*, major isomer); 30.3 (*s*, minor isomer I). FAB-MS (NBA): 486 (39, $[M+H]^+$), 470 (3, $M-Me]^+$), 408 (2, $M-C_6H_5]^+$), 396 (49, $M-Me_3SiO]^+$), 306 (96, $[M-CH(OSiMe_3)C_6H_5]^+$), 269 (6, $[C_6H_5CHCH(OSiMe_3)C_6H_5]^+$), 187 (100, $[M-MeNCH(CH(OSiMe_3)C_6H_5)C_6H_5]^+$), 179 (8, $[C_6H_5CHOSiMe_3]^+$), 171 (10, $[M-ON(Me)CH(CH(OSiMe_3)C_6H_5)C_6H_5]^+$), 73 (55, Me_3SiO^+)]. FAB-MS (NBA + KCl): 524 (16, $[M+K]^+$), 486 (37, $[M+H]^+$), 470 (5, $[M-Me]^+$), 408 (3, $[M-C_6H_5]^+$), 396 (45,$[M-Me_3SiO]^+$), 306 (86, $[M-CH(OSiMe_3)C_6H_5]^+$), 269 (6, $[C_6H_5CHCH(OSiMe_3)C_6H_5]^+$), 187 (100, $[M-MeNCH(CH(OSiMe_3)C_6H_5)C_6H_5]^+$), 179 (9, $[C_6H_5CHOSiMe_3]^+$), 171 (11, $[M-ON(Me)CH(CH(OSiMe_3)C_6H_5)C_6H_5]^+$), 73 (57, Me_3SiO^+). Anal. calc. for $C_{26}H_{40}N_3O_2PSi$ (485.69): C 64.30, H 8.30, N 8.65; found: C 64.14, H 8.26, N 8.58.

rac-trans-N-*Octahydro*-N*,1,3-trimethyl*-N-*{1,2,2-triphenyl-2-[(trimethylsilyl)oxy]ethyl}-2*H-*1,3,2-benzodiazaphosphol-2-amine 2-Oxide* (*rac*-**8**). With *rac*-**1** (143.5 mg, 0.467 mmol) and benzophenone/Me_3SiCl soln. (0.617M in THF, 0.617 mmol), according to *GP 1*. FC (AcOEt/EtOH 1:1; R_f 0.37) afforded 65 mg (35%) of *rac*-**8**, diastereoisomer ratio 86:14. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: −0.08 (*s*, Me_3Si); 0.8–1.3 (*m*, 2 CH_2); 1.52 (*d*, ^3J(P,H) = 9.5, 1 MeN); 1.6–1.8 (*m*, 2 CH_2); 1.68 (*d*, ^3J(P,H) = 12, 1 MeN); 2.15–2.65 (*m*, H–C(3a), H–C(7a)); 2.46 (*d*, ^3J(P,H) = 12, 1 MeN); 5.60 (*d*, ^2J(P,H) = 10, NC*H*Ph); 6.92–7.10 (*m*, 5 arom. H); 7.23–7.44 (*m*, 6 arom. H); 7.66–7.82 (*m*, 4 arom. H); minor isomer: −0.07 (*s*, Me_3Si); 2.65 (*d*, ^3J(P,H) = 12, 1 MeN); 5.59 (*d*, ^2J(P,H) = 10, NC*H*Ph). ^{13}C-NMR (75 MHz, {^{1}H}, $CDCl_3$): 2.27 (*s*, 3 C, Me_3Si); 24.21 (*s*); 24.28 (*s*); 26.74 (*d*, J(P,C) = 3.5); 28.12 (*s*); 28.28 (*s*); 28.58 (*d*, J(P,C) = 8.1); 29.26 (*d*, J(P,C) = 2.7); 63.20 (*d*, ^2J(P,C) = 8.1); 65.26 (*d*, ^2J(P,C) = 9.2); 66.06 (*d*, J(P,C) = 2.4); 88.59 (*d*, J(P,C) = 9.1); 126.5 (*s*, arom. C); 127.0 (*s*, arom. C); 127.1 (*s*, arom. C); 127.2 (*s*, arom. C); 127.5 (*s*, arom. C); 127.7 (*s*, arom. C); 128.2 (*s*, arom. C); 129.5 (*s*, arom. C); 131.3 (*s*, arom. C); 141.0 (*s*, C_{ipso}); 145.1 (*s*, C_{ipso}); 145.8 (*s*, C_{ipso}). ^{31}P-NMR (121 MHz, {^{1}H}, $CDCl_3$): 30.5 (*s*, major isomer); 31.1 (*s*, minor isomer). FAB-MS (NBA): 562 (5, $[M+H]^+$), 546 (2, $[M-Me]^+$), 488 (2, $[M-Me_3Si]^+$), 484 (3, $[M-C_6H_5]^+$), 472 (64, $[M-Me_3SiO]^+$), 306 (100, $[M-C(OSiMe_3)(C_6H_5)_2]^+$), 255 (20, $[(C_6H_5)_2COSiMe]^+$), 187 (86, $[M-MeNCH(C(OSi(Me_3)(C_6H_5)_2)C_6H_5]^+$), 73 (51, Me_3SiO^+). FAB-MS (NBA + KCl): 600 (5, $[M+K]^+$), 562 (3, $[M+H]^+$), 488 (2, $[M-Me_3Si]^+$), 484 (2, $[M-C_6H_5]^+$), 472 (33, $[M-Me_3SiO]^+$), 306 (71, $[M-C(OSiMe)_3)(C_6H_5)_2]^+$), 255 (21, $[(C_6H_5)_2COSiMe_3]^+$), 187 (95, $[M-MeNCH(C(OSiMe_3)(C_6H_5)_2)C_6H_5]^+$), 73 (100, Me_3SiO^+). HR-EI-MS (70 eV): 561.2913 (calc. 561.2940).

rac-trans-*Ethyl α-[Methyl(octahydro-1,3-dimethyl-2-oxido-2*H-*1,3,2-benzodiazophosphol-2-yl)amino]benzeneacetate* (*rac*-**9**). With *rac*-**1** (194.0 mg, 0.631 mmol) and ethyl carbonochloridate (0.954M in THF, 0.69 mmol), according to *GP 1*. FC (AcOEt; R_f 0.33) afforded 59.9 mg (25%) of *rac*-**9**, diastereoisomer ratio 87:13. Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 1.0–1.4 (*m*, 2 CH_2); 1.28 (*t*, ^3J = 7, *Me*CH_2O); 1.7–2.1 (*m*, 2 CH_2); 2.3–2.75 (*m*, H–C(3a), H–C(7a)); 2.40 (*d*, ^3J(P,H) = 12, 1 MeN); 2.42 (*d*, ^3J(P,H) = 7, 1 MeN); 2.65 (*d*, ^3J(P,H) = 10, 1 MeN); 4.32 (*q*, ^3J = 7, MeCH_2O); 5.73 (*d*, ^2J(P,H) = 9, NC*H*Ph); 7.27–7.43 (*m*, 5 arom. H); minor isomer: 5.78 (*d*, ^2J(P,H) = 8, NC*H*Ph). ^{13}C-NMR (75 MHz, {^{1}H}, $CDCl_3$): 14.14; 24.21; 24.24; 28.12; 28.16; 28.26; 28.51; 28.53; 28.58; 28.65; 28.96; 29.00; 60.76; 62.49; 62.55; 63.09; 63.18; 65.26; 65.36; 127.74; 128.32; 128.35; 128.94; 129.13; 136.34; 136.38; 172.43; 172.46. ^{31}P-NMR (121 MHz, {^{1}H}, $CDCl_3$), 29.9 (*s*, major isomer); 30.1 (*s*, minor isomer). EI-MS (70 eV): 379 (1, M^+), 306 (100, $[M-CO_2C_2H_5]^+$), 187 (71, $[M-CO_2C_2H_5-CHC_6H_5]^+$). FAB-MS (NBA): 380 (75, $[M+H]^+$), 379 (5, M^+), 306 (50, $[M-CO_2C_2H_5]^+$), 187 (100, $[M-MeNCH(CO_2C_2H_5)C_6H_5]^+$). FAB-MS (NBA + KCl): 418 (13, $[M+K]^+$), 380 (61, $[M+H]^+$), 379 (5, M^+), 306 (42, $[M-CO_2C_2H_5]^+$), 187 (100, $[M-MeNCH(CO_2C_2H_5)C_6H_5]^+$). HR-EI-MS (70 eV): 379.2044 (calc. 379.2024).

rac-trans-*α-[Methyl(octahydro-1,3-dimethyl-2-oxido-2*H*-1,3,2-benzodiazophosphol-2-yl)amino]*-N-*phenylbenzeneacetamide* (*rac*-**10**). With *rac*-**1** (140.1 mg, 0.456 mmol) and phenyl isocyanate (0.918M in THF, 0.55 mmol), according to *GP 1*. FC (AcOEt/EtOH 10:1; R_f 0.51) afforded 180.0 mg (94%) of *rac*-**10**, diastereoisomer ratio 80:20. Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 1.0–1.45 (*m*, 2 CH_2); 1.75–2.1 (*m*, 2 CH_2); 2.3–2.75 (*m*, H–C(3a), H–C(7a), 3 MeN); 5.66–5.92 (*m*, NC*H*Ph); 6.95–7.7 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, {^{1}H}, $CDCl_3$): 24.89; 28.86; 28.96; 29.42; 29.51; 29.79; 29.81; 63.51; 64.19; 64.25; 65.67; 65.74; 120.37; 120.50; 124.28; 128.32; 128.71; 129.02; 129.23; 129.29; 129.59; 129.81; 130.32; 137.40; 137.43; 139.40. ^{31}P-NMR (121 MHz, {^{1}H}, $CDCl_3$): 48.6 (*s*, minor isomer); 49.0 (*s*, major isomer). EI-MS (70 eV): 426 (0.3, M^+), 306 (100, $[M-CONHC_6H_5]^+$), 187 (73, $[M-CONHC_6H_5-CHC_6H_5]^+$). FAB-MS (NBA): 427 (56, $[M+H]^+$), 426 (5, M^+), 306 (100, $[M-CONHC_6H_5]^+$), 187 (100, $[M-MeNCH(CO_2C_2H_5)C_6H_5]^+$), 120 (94, $CONHC_6H_5^+$). FAB-MS (NBA + KCl): 465 (20, $[M+K]^+$), 427 (46, $[M+H]^+$), 426 (5, M^+), 306 (85, $[M-CONHC_6H_5]^+$), 187 (100, $[M-MeNCH(CO_2C_2H_5)C_6H_5]^+$), 120 (96, $CONHC_6H_5^+$). Anal. calc. for $C_{23}H_{31}N_4O_2P\cdot H_2O$ (444.51): C 62.15, H 7.48, N 12.60; found: C 61.83, H 7.44, N 11.73.

General Procedure (GP 2) for Trapping Reactions with Aldehydes in the Presence of Lithium Bromide. To a soln. of **1** (*ca*. 0.5 mmol) in dry Et_2O (3 ml), BuLi (1.1 equiv.) in hexane was added at −78°. After stirring for 1 h at −78°, 4 equiv. of dry LiBr were added. Again after stirring for 1 h at −78°, a soln. of the aldehyde (1 equiv.) in Et_2O (1 ml) was added dropwise. After decolorization of the deep red suspension, the mixture was treated with sat. $NaHCO_3$ soln. and extracted with AcOEt. The org. layer was dried ($NaSO_4$) and evaporated and the residue purified by FC to afford the diastereoisomeric products, which were recrystallized in hexane. The diastereomer ratios were determined by integration of the ^{31}P-NMR spectra of the crude products.

rac-trans-*Octahydro-1,3-dimethyl-α-phenyl-2*H*-1,3,2-benzodiazaphosphole-2-methanol 2-Oxide* (*rac*-**12**). With *rac*-**1** (180.1 mg, 0.586 mmol), LiBr (254.5 mg, 2.93 mmol), and benzaldehyde (0.97M in Et_2O, 0.878 mmol), according to *GP 2*. FC (AcOEt/EtOH 10:1) afforded 125.9 mg (52%) of *rac*-**12**, diastereoisomer ratio 55:45. Colorless solid. After recrystallization from hexane, the diastereoisomer ratio was 82:18. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 0.88–1.35 (*m*, 2 CH_2); 1.73–2.05 (*m*, 2 CH_2); 2.35 (*d*, ^3J(P,H) = 11.3, 1 MeN); 2.59 (*d*, ^3J(P,H) = 9.8, 1 MeN); 2.2–2.71 (*m*, H–C(3a), H–C(8a)); 3.6, 3.8 (2 br., *s*, CHO*H*); 5.17 (*d*, ^2J(P,H) = 10.4, C*H*OH); 7.24–7.37 (*m*, 2 H_m, H_p); 7.43–7.49 (*m*, 2 H_o); minor isomer: 2.22 (*d*, ^3J(P,H) = 11.0, 1 MeN); 2.54 (*d*, ^3J(P,H) = 9.7, 1 MeN); 4.90 (*d*, ^2J(P,H) = 7.8, C*H*OH). ^{13}C-NMR (75 MHz, {^{1}H}, $CDCl_3$): 24.06 (*s*); 24.09 (*s*); 24.15 (*s*); 24.27 (*s*); 27.71 (*d*, ^3J(P,C) = 6.9); 27.95 (*d*, ^3J(P,C) = 6.3); 28.05 (*d*, ^2J(P,C) = 4.0, 1 MeN); 28.28 (*d*, ^3J(P,C) = 2.5); 28.35 (*d*, ^3J(P,C) = 5.4); 28.43 (*d*, ^2J(P,C) = 4.3, 1 MeN); 29.49 (*s*, 1 MeN); 30.19 (*s*, 1 MeN); 63.75 (*d*, ^2J(P,C) = 7.2); 64.19 (*d*, ^2J(P,C) = 6.4); 64.40 (*d*, ^2J(P,C) = 4.2); 64.66 (*d*, ^2J(P,C) = 4.2); 70.80 (*d*, ^1J(P,C) = 122.4, CHOH); 71.59 (*d*, ^1J(P,C) = 122.3, CHOH); 126.4 (*d*, ^3J(P,C) = 4.4 arom. C); 127.1 (*d*, ^3J(P,C) = 5.0 arom. C); 127.3 (*d*, ^5J(P,C) = 2.9, C_p); 127.5 (*d*, ^5J(P,C) = 3.5, C_p); 127.8 (*d*, ^5J(P,C) = 2.5, 2 arom. C); 128.0 (*d*, J(P,C) = 2.6, 2 arom. C); 137.5 (*d*, J(P,C) = 2.2, C_{ipso}); 137.7 (*d*, J(P,C) = 2.8, C_{ipso}). ^{31}P-NMR (121 MHz, {^{1}H}, $CDCl_3$): 36.9 (*s*, minor isomer); 37.7 (*s*, major isomer). EI-MS (70 eV): 294 (1, M^+), 187 (100, $[M-CHOHC_6H_5]^+$), 77 (17, $C_6H_5^+$). FAB-MS (NBA): 295 (100, $[M+H]^+$), 277 (7, $[M-OH]^+$), 204 (8, $[M-CHC_6H_5]^+$), 187 (52, $[M-CHOHC_6H_5]^+$), 171 (52, $[M-OCHOHC_6H_5]^+$), 91 (3, $CH_2C_6H_5^+$). FAB-MS (NBA + KCl): 333 (36, $[M+K]^+$), 295 (100, $[M+H]^+$), 277 (8, $[M-OH]^+$), 204 (8, $[M-CHC_6H_5]^+$), 187 (60, $[M-CHOHC_6H_5]^+$), 171 (53, $[M-OCHOHC_6H_5]^+$), 91 (5, $[CH_2C_6H_5^+$). Anal. calc. for $C_{15}H_{23}N_2O_2P$ (294.34): C 61.21, H 7.88, N 9.52; found: C 61.02, H 7.77, N 9.11.

rac-trans-*Octahydro-α-(4-methoxyphenyl)-1,3-dimethyl-2*H*-1,3,2-benzodiazaphosphole-2-methanol 2-Oxide* (*rac*-**13**). With *rac*-**1** (197.3 mg, 0.642 mmol), LiBr (223.0 mg, 2.57 mmol), and 4-methoxybenzaldehyde (0.75M in Et_2O, 0.975 mmol), according to *GP 2*. FC (AcOEt/EtOH 10:1) afforded 104 mg (32%) of *rac*-**13**, diastereoisomer ratio 53:47. Colorless solid. After recrystallization from hexane, the diastereoisomer ratio was 96:4. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–1.35 (*m*, 2 CH_2); 1.72–2.04 (*m*, 2 CH_2); 2.23 (*d*, ^3J(P,H) = 11.0, 1 MeN); 2.29 (*d*, ^3J(P,H) = 11.2, 1 MeN); 2.55 (*d*, ^3J(P,H) = 9.6, 1 MeN); 2.61 (*d*, ^3J(P,H) = 9.9, 1 MeN); 2.3–2.7 (*m*, H–C(3a), H–C(7a)); 3.42, 3.66 (2 br., *s*, CHO*H*); 4.82, 5.12 (2*d*, ^2J(P,H) = 6.6, 9.1, C*H*OH); 6.87 (*d*, ^3J = 8.5, 2 H_m); 7.34–7.41 (*m*, 2 H_o). ^{13}C-NMR (75 MHz, {^{1}H}, $CDCl_3$): 24.07 (*s*); 24.08 (*s*); 24.16 (*s*); 24.29 (*s*); 27.74 (*d*, ^3J(P,C) = 6.9); 27.95 (*s*); 28.10 (*s*, MeN); 28.35 (*s*); 28.41 (*d*, ^3J(P,C) = 8.0); 28.55 (*s*, MeN); 29.58 (*s*, MeN); 30.34 (*s*, MeN); 55.23 (*s*, MeO); 63.80 (*d*, ^2J(P,C) = 6.9); 64.24 (*d*, ^2J(P,C) = 6.0); 64.46 (*d*, ^2J(P,C) = 4.2); 64.75 (*d*, ^2J(P,C) = 4.0); 70.34 (*d*, ^1J(P,C) = 126.2, CHOH); 71.18 (*d*, ^1J(P,C) = 124.7, CHOH); 113.4 (*d*, ^4J(P,C) = 6.6, 2 C); 127.5 (*d*, ^4J(P,C) = 4.3, 2 C); 128.4 (*d*, ^3J(P,C) = 5.0, 2 C); 129.6 (*s*); 129.7 (*s*); 159.0 (*d*, ^5J(P,C) = 3.0); 159.1 (*d*, ^5J(P,C) = 2.8). ^{31}P-NMR (121 MHz, {^{1}H}, $CDCl_3$): 36.8 (*s*, major isomer); 38.4 (*s*, minor isomer). EI-MS (70 eV): 324 (10, M^+), 307 (3, $[M-OH]^+$), 188 [100, $[M-CHOC_6H_4OMe]^+$), 187 (70, $[M-CHOHC_6H_4OMe]^+$), 136 (74, $[CHOC_6H_4OMe]^+$), 120 (16, $[CHC_6H_4OMe]^+$), 107 (7, $C_6H_4OMe^+$). FAB-MS (Thio): 325 (39, $[M+H]^+$), 308 (10, $[M-O]^+$), 307 (7,

$[M-OH]^+$), 187 (17, $[M-CHOHC_6H_4OMe]^+$), 171 (33, $[M-OCHOHC_6H_4OMe]^+$), 45 (100). Anal. calc. for $C_{16}H_{25}N_2O_3P$ (324.36): C 59.25, H 7.77, N 8.64; found: C 59.13, H 7.72, N 8.57.

rac-trans-*Octahydro-1,3-dimethyl-α-(4-nitrophenyl)-2*H-*1,3,2-benzodiazaphosphole-2-methanol 2-Oxide* (*rac*-**14**). With *rac*-**1** (190.2 mg, 0.619 mmol), LiBr (223.0 mg, 2.57 mmol), and 4-nitrobenzaldehyde (500 mg, 3.31 mmol), according to *GP 2*. FC (AcOEt/EtOH 10 : 1) afforded 107.6 mg (51%) of *rac*-**14**, diastereomer ratio 54 : 46. Colorless solid. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 0.91–1.37 (*m*, 2 CH_2); 1.75–2.05 (*m*, 2 CH_2); 2.31 (*d*, ^3J(P,H) = 11.2, 1 MeN); 2.43–2.51 (*m*, H–C(3a), H–C(7a)); 2.51 (*d*, ^3J(P,H) = 9.7, 1 MeN); 4.0 (br. *s*, CHO*H*); 5.06 (*d*, ^2J(P,H) = 9.9, C*H*OH); 7.65–7.71 (*m*, 2 H_o); 8.21 (*d*, ^3J = 8.6, 2 H_m); minor isomer: 2.33 (*d*, ^3J(P,H) = 11.4, 1 MeN); 2.61 (*d*, ^3J(P,H) = 9.9, 1 MeN); 2.61–2.70 (*m*, H–C(3a), H–C(7a)); 3.7 (br. *s*, CHO*H*); 5.29 (*d*, ^2J(P,H) = 12.7, C*H*OH). ^{13}C-NMR (75 MHz, {^{1}H}, $CDCl_3$): major isomer: 23.97 (*s*); 24.01 (*s*); 24.09 (*s*); 24.18 (*s*); 27.72 (*d*, ^3J(P,C) = 7.1); 27.94 (*d*, ^3J(P,C) = 7.0); 27.97 (*d*, ^2J(P,C) = 4.6, MeN); 28.21 (*s*); 28.38 (*d*, ^3J(P,C) = 9.0); 28.39 (*s*, MeN); 29.75 (*s*, MeN); 63.90 (*d*, ^2J(P,C) = 7.2); 64.60 (*d*, ^2J(P,C) = 4.4); 71.17 (*d*, ^1J(P,C) = 119.5, CHOH); 123.1 (*d*, ^4J(P,C) = 2, 2 C); 127.7 (*d*, ^3J(P,C) = 4.6, 2 C); 145.6 (*m*); 147.1 (*m*); minor isomer: 30.16 (*s*, MeN); 64.38 (*d*, ^2J(P,C) = 5.7); 64.75 (*d*, ^2J(P,C) = 4.8); 70.44 (*d*, ^1J(P,C) = 122.1, CHOH); 122.9 (*d*, ^4J(P,C) = 3.1, 2 C); 127.2 (*d*, ^3J(P,C) = 4.1, 2 C). ^{31}P-NMR (121 MHz, {^{1}H}, $CDCl_3$): 35.9 (*s*, major isomer); 36.4 (*s*, minor isomer). EI-MS (70 eV): 339 (5, M^+), 309 (12, $M-NO]^+$), 204 (40, $[M-CHC_6H_4NO_2]^+$), 187 (100, $[M-CHOHC_6H_4NO_2]^+$), 151 (21, $CHOC_6H_4NO_2^+$). FAB-MS (Thio): 340 (70, $[M+H]^+$), 324 (6, $[M-Me]^+$), 308 (100, $[M-O_2]^+$), 187 (50, $[M-CHOHC_6H_4NO_2]^+$), 171 (41, $[M-OCHOHC_6H_4NO_2]^+$), 45 (94). HR-EI-MS (70 eV): 339.1325 (calc. 339.1348).

rac-trans-*Octahydro-α-(2-methoxyphenyl)-1,3-dimethyl-2*H-*1,3,2-benzodiazaphosphole-2-methanol 2-Oxide* (*rac*-**15**). With *rac*-**1** (176.9 mg, 0.576 mmol), LiBr (200.1 mg, 2.30 mmol), and 2-methoxybenzaldehyde (1.35M in Et_2O, 0.878 mmol), according to *GP 2*. FC (AcOEt/EtOH 10 : 1) afforded 103.2 mg (55%) of *rac*-**15**, diastereoisomer ratio 62 : 38. Colorless solid. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 0.79–1.38 (*m*, 2 CH_2); 1.73–2.07 (*m*, 2 CH_2); 2.01 (*d*, ^3J(P,H) = 10.8, 1 MeN); 2.32–2.7 (*m*, H–C(3a), H–C(7a)); 2.67 (*d*, ^3J(P,H) = 10.4, 1 MeN); 3.82 (*s*, MeO); 5.30, 5.46 (2*d*, ^2J(P,H) = 8.7, 10.6, C*H*OH); 6.82–7.01 (*m*, 2 arom. H); 7.21–7.51 (*m*, 2 arom. H); minor isomer: 2.39 (*d*, ^3J(P,H) = 11.1, 1 MeN); 2.64 (*d*, ^3J(P,H) = 9.6, 1 MeN); 3.84 (*s*, MeO). ^{13}C-NMR (75 MHz, {^{1}H}, $CDCl_3$): major isomer: 24.7 (*s*); 24.22 (*s*); 27.67 (*d*, ^3J(P,C) = 7.9); 28.33 (*d*, ^3J(P,C) = 9.6); 28.48 (*d*, ^2J(P,C) = 4.4, MeN); 28.97 (*s*, MeN); 55.25 (*s*, MeO); 63.35 (*d*, ^2J(P,C) = 7.3); 64.7 (*d*, ^2J(P,C) = 5.4); 64.69 (*d*, ^1J(P,C) = 120.6, CHOH); 109.9 (*s*); 120.5 (*s*); 126.9 (*d*, ^2J(P,C) = 3); 127.9 (*d*, *J*(P,C) = 4.1, arom. C); 128.4 (*d*, *J*(P,C) = 3.2, arom. C); 155.9 (*d*, ^3J(P,C) = 4.9); minor isomer (due to signal overlap, not all resonances could be detected): 24.30 (*s*); 27.98 (*d*, ^3J(P,C) = 6.9); 28.7 (*d*, ^2J(P,C) = 4.4, MeN); 28.57 (*d*, ^3J(P,C) = 9); 30.36 (*s*, MeN); 55.38 (*s*, MeO); 64.10 (*d*, ^2J(P,C) = 5); 64.64 (*d*, ^2J(P,C) = 4.3); 67.59 (*d*, ^1J(P,C) = 127.5, CHOH); 110.5 (*s*); 120.6 (*s*); 125.9 (*s*); 128.2 (*d*, *J*(P,C) = 4.6, arom. C); 128.5 (*d*, *J*(P,C) = 3.1, arom C); 156.7 (*d*, ^3J(P,C) = 5). ^{31}P-NMR (121 MHz, {^{1}H}, $CDCl_3$): 37.9 (*s*, minor isomer); 38.2 (*s*, major isomer). EI-MS (70 eV): 324 (20, M^+), 188 (100, $[M-CHOC_6H_4OMe]^+$), 188 (100, $[M-CHOC_6H_4OMe]^+$), 141 (84), 136 (43, $[CHOC_6H_4OMe]^+$). FAB-MS (NBA): 325 (100, $[M+H]^+$), 204 (8, $[M-CHC_6H_4OMe]^+$), 187 (58, $[M-CHOHC_6H_4OMe]^+$), 171 (82, $[M-OCHOHC_6H_4OMe]^+$). FAB-MS (NBA + KCl): 363 (37, $[M+K]^+$), 325 (100, $[M+H]^+$), 204 (11; $[M-CHC_6H_4OMe]^+$), 187 (68, $[M-CHOHC_6H_4OMe]^+$), 171 (87, $[M-OCHOHC_6H_4OMe]^+$). HR-EI-MS (70 eV): 324.1580 (calc. 324.1603).

rac-trans-*α-(1,1-Dimethylethyl)-octahydro-1,3-dimethyl-2*H-*1,3,2-benzodiazaphosphole-2-methanol 2-Oxide* (*rac*-**16**). With *rac*-**1** (172.0 mg, 0.560 mmol), LiBr (188.2 mg, 2.20 mmol), and pivalaldehyde (= 2.2-dimethylpropanal; 1.51M in Et_2O; 0.604 mmol), according to *GP 2*. FC (AcOEt/EtOH 10 : 1) afforded 49.6 mg (32%) of *rac*-**16**, diastereoisomer ratio 77 : 23. Colorless solid. After recrystallization from hexane, the diastereoisomer ratio was 80 : 20. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 1.02–1.38 (*m*, 2 CH_2); 1.07 (*s*, Me_3C); 1.82–2.04 (*m*, 2 CH_2); 2.56–2.73 (*m*, 2 MeN, H–C(3a), H–C(7a)); 3.42 (*d*, ^2J(P,H) = 4.4, C*H*OH); minor isomer: 1.11 (*s*, Me_3C); 4.63 (*d*, ^2J(P,H) = 8.3, C*H*OH). ^{13}C-NMR (75 MHz, {^{1}H}, $CDCl_3$): major isomer: 24.02 (*s*); 24.33 (*s*); 27.05 (*s*, 3 C, *Me*$_3$C); 27.97 (*d*, ^3J(P,C) = 7.3); 28.54 (*d*, ^3J(P,C) = 8.9); 28.66 (*d*, ^2J(P,C) = 3.3, MeN); 30.92 (*s*, MeN); 34.65 (*s*, Me_3C); 62.65 (*d*, ^2J(P,C) = 7.8); 65.71 (*d*, ^2J(P,C) = 3.7); 76.96 (*d*, ^1J(P,C) = 118.8, CHOH); minor isomer: 24.09 (*s*); 24.52 (*s*); 26.98 (*s*, *Me*$_3$C); 28.41 (*s*, MeN); 28.52 (*d*, ^3J(P,C) = 10.5); 29.05 (*d*, ^3J(P,C) = 10.3); 31.60 (*s*, MeN); 35.01 (*s*, Me_3C); 63.75 (*d*, ^2J(P,C) = 6.4); 66.67 (*d*, ^2J(P,C) = 3.0); 74.95 (*d*, ^1J(P,C) = 114.1, CHOH). ^{31}P-NMR (121 MHz, {^{1}H}, $CDCl_3$): 41.0 (*s*, major isomer); 43.3 (*s*, minor isomer). EI-MS (70 eV): 217 (6, $[M-Me_3C]^+$), 187 (100, $[M-CHOHCCMe_3]^+$), 141 (66), 57 (28, Me_3C^+). FAB-MS (NBA): 275 (100, $[M+H]^+$), 187 (38, $[M-CHOHCMe_3]^+$), 171 (34, $[M-OCHOHCMe_3]^+$), 57 (10, Me_3C^+). Anal. calc. for $C_7H_{27}N_2O_2P$ (274.35): C 56.91, H 9.92, N 10.21; found: C 56.84, H 9.66, N 10.08.

*NMR Investigation of Octahydro-*N*,1,3-trimethyl-*N*-(phenylmethyl)-2*H-*1,3,2-benzodiazaphosphol-2-amine 2-Oxide* (*ent*-**1**) *in (D$_8$)THF.* (*S*)-**1** (40 mg, 0.13 mmol) was dissolved in dry (D_8)THF (0.7 ml, 0.19M) and

measured at 25°. ^{1}H-NMR (600 MHz, (D_8)THF, δ(CDHO) 3.58): 1.08–1.47 (*m*, CH_2(5), CH_2(6)); 1.70–1.85 (*m*, CH_2(4)); 1.94–2.04 (*m*, CH_2(7)); 2.37 (*d*, ^3J(P,H) = 11.4, 1 MeN); 2.41 (*d*, ^3J(P,H) = 10.4, 1 MeN); 2.43 (*d*, ^3J(P,H) = 9.4, 1 MeN); 2.47–2.70 (*m*, H–C(3a), H–C(8a)); 4.17 (*dd*, ^2J = 14.4, ^3J(P,H) = 6.9, 1 H, NC$H_2$$C_6H_5$); 4.24 (*dd*, ^2J = 14.4, ^3J(P,H) = 8.7, 1 H, NC$H_2$$C_6H_5$); 7.17–7.37 (*m*, 5 arom. H). ^{13}C-NMR (150 MHz, {^{1}H}, (D_8)THF, δ(CD_2O) 67.29; due to signal overlap, not all resonances could be detected): 28.04 (*d*, ^2J(P,C) = 2.9, MeN(ring)); 29.20 (*d*, ^3J(P,C) = 10.4); 29.35 (*s*, MeN(ring)); 29.70 (*d*, ^3J(P,C) = 7.7); 32.88 (*d*, ^2J(P,C) = 2.9, MeN(exocyclic)); 53.80 (*d*, ^2J(P,C) = 4.4, CH_2N); 64.48 (*d*, ^2J(P,C) = 8.7); 65.86 (*d*, ^2J(P,C) = 9.2); 127.6 (*s*, C_p); 128.8 (*s*, 2 arom. C); 129.2 (*s*, 2 arom. C); 140.6 (*d*, ^2J(P,C) = 3.3, C_{ipso}). ^{31}P-NMR (242 MHz, {^{1}H}, (D_8)THF): 30.7 (*s*).

^{1}H-, ^{7}Li-, ^{13}C-, and ^{31}P-NMR Investigation of ent-*Lithium [Methyl(octahydro-1,3-dimethyl-2-oxido-2*H*-1,3,2-benzodiazaphosphol-2-yl)amino]phenylmethanide* (*ent*-**2**). (*S*)-**1** (82 mg, 0.267 mmol) was dissolved in dry (D_8)THF (1 ml, 0.27M) at −78° and added to BuLi (1.1 equiv.). The soln. was warmed to r.t. and afterwards frozen in liq. N_2 under vacuum. The degassed purple soln. was transferred under Ar to a flame-dried NMR tube equipped with a three-way stop cock, frozen in liq. N_2 and sealed under vacuum. ^{1}H-NMR (300 MHz, (D_8)THF, δ (CDHO) 3.58, 25°): 0.8–1.0 (*m*, 3 H); 1.0–1.45 (*m*, 6 H); 1.45–1.85 (*m*, 3 H); 1.85–2.15 (*m*, 2 H); 2.15 (*d*, *J* = 6.2, 1 H); 2.2–2.7 (*m*, 5 H); 7.0–7.4 (*m*, 5 arom. H); cooling of the sample up to −60° had no significant effect on the δs and the line shape; at −110°, strong broadening of all signals. ^{13}C-NMR (75 MHz, {^{1}H}, (D_8)THF, δ, (CD_2O) 67.29, 25°; due to signal overlap, not all resonances could be detected, impurities (butane and hexane) showed resonances at δ 14); 14.11 (*s*, Me); 14.41 (*s*, Me); 23.70 (*s*, CH_2); 25.53 (*s*, CH_2); 25.72 (*s*, CH_2); 29.42 (*s*, CH_2); 30.5 (br. *s*, CH_2); 30.9 (br. *s*, CH_2); 34.95 (*s*, Me); 39.23 (*s*, CH_2); 64.4 (br. *s*); 66.60 (*s*, NCHC_6H_5); 71.5 (br. *s*); 127.3 (*s*, C_p); 128.1 (*s*, 2 arom. C); 128.8 (*s*, 2 arom. C); 146.0 (*d*, ^2J(P,C) = 3.3, C_{ipso}). ^{13}C-NMR (75 MHz, (D_8)THF, δ (CD_2O) 67.29, 25°; due to signal overlap, not all resonances could be detected, impurities (butane and hexane) showed resonances at δ 14): 14.11 (*q*, ^1J(C,H) = 125, Me); 23.70 (*t*, ^1J(C,H) = 120, CH_2); 34.95 (*q*, ^1J(C,H) = 135, Me); 39.23 (*t*, ^1J(C,H) = 122.5, CH_2); 64.4 (br. *d*, ^1J(C,H) = 135.2, C(3a), C(7a)); 66.60 (*d*, ^1J(C,H) = 129, NCHC_6H_5); 71.5 (br. *d*, ^1J(C,H) = 144.2, C(3a), C(7a)); 127.3 (*d*, ^1J(C,H) = 162.5, C_p); 128.1 (*d*, ^1J(C,H) = 160, 2 arom. C); 128.8 (*d*, ^1J(C,H) = 162.5, 2 arom. C). ^{13}C-NMR (100 MHz, {^{1}H}, (D_8)THF, δ (CD_2O) 67.29, −108°; due to signal overlap, not all resonances could be detected, impurities (butane and hexane) showed resonances at δ 14): 14.88 (*s*, Me); 15.01 (*s*, Me); 24.25 (*s*, CH_2); 26.19 (*s*, CH_2); 29.86 (*s*, CH_2); 30.5 (br. *s*, CH_2); 31.2 (br. *s*, CH_2); 35.29 (*s*, Me); 40.33 (*s*, CH_2); 64.4 (br. *s*); 66.80 (*s*, NCHC_6H_5); 72.0 (br. *s*); 127.5 (*s*, C_p); 128.1 (*s*, 2 arom. C); 128.9 (*s*, 2 arom. C); 145.9 (*s*, C_{ipso}). ^{31}P-NMR (121 MHz, {^{1}H}, (D_8)THF, 25°): 31.6 (*s*); 34.3 (*s*); 1 : 1. ^{31}P-NMR (121 MHz, {^{1}H}, (D_8)THF, −108°): 4.4 (*s*); 31.7 (br. *s*); 33.9 (*s*); ratio 5 : 20 : 1. ^{7}Li-NMR (155 MHz, (D_8)THF, 25°): −0.22 (*s*). ^{7}Li-NMR (155 MHz, (D_8)THF, −108°): −0.51 (*s*).

REFERENCES

[1] S. R. Wilson, M. F. Price, *Synth. Commun*. **1982**, *12*, 657; O. Bortolini, F. D. Furia, G. Modena, A. Schionato, *J. Mol. Catal*. **1986**, *35*, 47; B. Burns, N. P. King, H. Tye, J. R. Studley, M. Gamble, M. Wills, *J. Chem. Soc., Perkin Trans. 1* **1998**, 1027.

[2] C. P. Mihal, Jr., *Am. Ind. Hyg. Assos. J.* **1987**, *48*, 997.

[3] S. E. Denmark, S. B. D. Winter, X. Su, K.-T. Wong, *J. Am. Chem. Soc*. **1996**, *118*, 7404; S. E. Denmark, K.-T. Wong, R. A. Stavenger, *J. Am. Chem. Soc.* **1997**, *119*, 2333; S. E. Denmark, S. B. D. Winter, *Synlett* **1997**, 1087; S. E. Denmark, R. A. Stavenger, K.-T. Wong, *Tetrahedron* **1998**, *54*, 10389; S. E. Denmark, P. A. Barsanti, K.-T. Wong, R. A. Stavenger, *J. Org. Chem*. **1998**, *63*, 2428; S. E. Denmark, R. A. Stavenger, K.-T. Wong, *J. Org. Chem*. **1998**, *63*, 918.

[4] H. Normant, *Bull. Soc. Chim. Fr.* **1967**, 791; R. R. Dykstra, in 'Encyclopedia of Reagents for Organic Synthesis', Ed. L. A. Paquette, John Wiley & Sons, Chichester, New York, 1995, Vol. 4, p. 2668.

[5] S. Hanessian, D. Delorme, S. Beaudoin, Y. Leblanc, *J. Am. Chem. Soc*. **1984**, *106*, 5754; F. Bélanger-Gariépy, D. Delorme, S. Hanessian, F. Brisse, *Acta Crystallogr. Sect. C* **1986**, *42*, 856; F. Bélanger-Gariépy, Y. L. Bennani, s. Hanessian, F. Brisse, *ibid*. **1989**, *45*, 289; F. Bélanger-Gariépy, Y. L. Bennani, S. Beaudoin, S. Hanessian, *ibid*. **1992**, *48*, 1533; M. Simard, S. Beaudoin, S. Hanessian, *ibid*. **1992**, *48*, 1535; J. F. Larrow, E. N. Jacobsen, *J. Org. Chem.* **1994**, *59*, 1939; S. Hanessian, D. Andreotti, A. Gomtsyan, *J. Am. Chem. Soc*. **1995**, *117*, 10393; Y. L. Bennani, S. Hanessian, *Tetrahedron Lett*. **1996**, *52*, 13837.

[6] H. Normant, T. Curvigny, G. J. Martin, *Bull. Soc. Chim. Fr.* **1969**, 1605; P. Savignac, M. Dreux, Y. Leroux, *Tetrahedron Lett*. **1974**, *15*, 2651; P. Savignac, P. Coutrot, Y. Leroux, *C. R. Acad. Sci. Ser. C* **1974**, 609; P.

Savignac, G. Lavielle, *J. Organomet. Chem.* **1974**, *72*, 361; P. Savignac, Y. Leroux, H. Normant, *Tetrahedron* **1975**, *31*, 877; P. Savignac, M. Dreux, *Tetrahedron Lett.* **1976**, *15*, 2025; D. Seebach, J.-J. Lohmann, M. A. Syfrig, M. Yoshifuji, *Tetrahedron* **1983**, *39*, 1963.

[7] J. F. K. Müller, B. Spingler, M. Zehnder, *Synlett* **1997**, 1059; J. F. K. Müller, B. Spingler, M. Zehnder, *J. Organomet. Chem.* **1998**, *570*, 293.

[8] D. Barr, W. Clegg, R. E. Mulvey, R. Snaith, *J. Chem. Soc., Chem. Commun.* **1984**, 79; D. Barr, M. J. Doyle, R. E. Mulvey, P. R. Raithby, D. Reed, R. Snaith, D. S. Wright, *ibid.* **1989**, 318; P. R. Raithby, D. Reed, R. Snaith, D. S. Wright, *Angew. Chem. Int. Ed.* **1991**, *30*, 1011; F. H. Allen, K. O., *Chem. Design Automat. News* **1993**, *8*, 31.

[9] G. Boche, A. Opel, M. Marsch, K. Harms, F. Haller, J. C. W. Lohrenz, C. Thümmler, W. Koch, *Chem. Ber.* **1992**, *125*, 2265; G. Boche, M. Marsch, J. Harbach, K. Harms, B. Ledig, J. C. W. Lohrenz, H. Ahlbrecht, *Chem. Ber.* **1993**, *126*, 1887; G. Boche, J. C. W. Lohrenz, A. Opel, in 'Lithium Chemistry', Eds. A.-M. Sapse, P. v. R. Schleyer, Wiley, New York, 1995, p. 195.

[10] H. Ahlbrecht, H. Dollinger, *Tetrahedron Lett.* **1984**, *25*, 1353; H. Ahlbrecht, J. Harbach, T. Hauck, H.-O. Kalinowski, *Chem. Ber.* **1992**, *125*, 1753; H. Ahlbrecht, J. Harbach, R. W. Hoffmann, T. Ruhland, *Liebigs Ann.* **1995**, 211; H. Ahlbrecht, J. Harbach, H.-O. Kalinowski, A. Lang, G. Maier, *Chem. Ber./Recueil* **1997**, *130*, 683.

[11] D. Seebach, R. Amstutz, J. D. Dunitz, *Helv. Chim. Acta* **1981**, *64*, 2622; D. Seebach, *Angew. Chem.* **1988**, *100*, 1685; C. Reichardt, 'Solvents and Solvent Effects in Organic Chemistry', 2nd edn., VCH, Weinheim, 1988; E. A. Loupy, b. Tchoubar, 'Salt Effects in Organic and Organometallic Chemistry', VCH, Weinheim, 1992; D. Seebach, A. K. Beck, A. Studer, in 'Modern Synthetic Methods', Vol. 7. Eds. B. Ernst and C. Leumann, VCHA and VCH, Basel and Weinheim, 1995, pp. 3.

[12] D. V. Patel, K. Rielly-Gauvin, D. E. Ryono, *Tetrahedron Lett.* **1990**, *31*, 5587; D. V. Patel, K. Rielly-Gauvin, D. E. Ryono, *ibid.* **1990**, *31*, 5591; M. L. Moore, G. B. Dreyer, *Perspect. Drug Discovery Des.* **1993**, *1*, 85; K. J. Koeller, N. P. Rath, C.-D. Spilling, *Acta Crystallogr., Sect. C* **1993**, *49*, 1547; V. J. Blazis, K. J. Koeller, N. P. Rath, C. D. Spilling, *ibid.* **1995**, *51*, 86.

[13] D. Seebach, J. Hansen, P. Seiler, J. M. Gromek, *J. Organomet. Chem.* **1985**, *285*, 1; G. Boche, M. Monde, J. Harbach, K. Harms, B. Ledig, F. Schubert, J. C. W. Lohrenz, H. Ahlbrecht, *Chem. Ber.* **1993**, *126*, 1887.

[14] D. Armstrong, D. Barr, M. G. Davidson, G. Hutton, P. O'Brien, R. Snaith, S. Warren, *J. Organomet. Chem.* **1997**, *529*, 29.

[15] P. Beak, D. B. Reitz, *Chem. Rev.* **1978**, *78*, 275; P. Beak, W. J. Zjdel, D. B. Reitz, *ibid.* **1984**, *84*, 471.

[16] W. Zarges, M. Marsch, K. Harms, F. Haller, G. Frenking, G. Boche, *Chem. Ber.* **1991**, *124*, 861; S. E. Denmark, R. L. Dorow, *J. Am. Chem. Soc.* **1990**, *112*, 864; S. E. Denmark, P. C. Miller, S. R. Wilson, *J. Am. Chem. Soc.* **1991**, *113*, 1468; S. E. Denmark, K. A. Swiss, S. R. Wilson, *J. Am. Chem. Soc.* **1993**, *115*, 3826; S. E. Denmark, K. A. Swiss, S. R. Wilson, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2515; J. E. Davies, R. P. Davies, L. Dunbar, P. R. Raithby, M. G. Russell, R. Snaith, S. Warren, A. E. H. Wheatley, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2334.

[17] M. Kranz, S. E. Denmark, K. A. Swiss, S. R. Wilson, *J. Org. Chem.* **1996**, *61*, 8551; S. E. Denmark, K. A. Swiss, P. C. Miller, S. R. Wilson, *Heteroat. Chem.* **1998**, *9*, 209.

[18] D. Seebach, V. Prelog, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 654.

[19] M. Drescher, F. Hammerschmidt, H. Kählig, *Synthesis* **1995**, 1267; C. Meier, W. H. G. Laux, J. W. Bats, *Liebigs Ann.* **1995**, 1963; G. Eidenhammer, F. Hammerschmidt, *Synthesis* **1996**, 748; D. Green, S. Elgendy, G. Patel, J. A. Baban, E. Skordalakes, W. Husman, V. V. Kakkar, J. Deadman, *Tetrahedron* **1996**, *52*, 10215; C. Qian, T. Huang, C. Zhu, J. Sun, *J. Chem. Soc., Perkin Trans. 1* **1998**, 2097.

[20] R. W. Hoffmann, W. Klute, *Chem. – Eur. J.* **1996**, *2*, 694; C. Guéguen, P. O'Brien, H. R. Powell, P. R. Raithby, S. Warren, *J. Chem. Soc., Perkin Trans. 1* **1998**, 3405.

[21] A. I. Meyers, L. M. Fuentes, Y. Kubota, *Tetrahedron* **1984**, *40*, 1361; P. Beak, W. K. Lee, *J. Org. Chem.* **1993**, *58*, 1109; W. H. Pearson, A. C. Lindbeck, J. W. Kampf, *J. Am. Chem. Soc.* **1993**, *115*, 2622.

[22] V. J. Blazis, K. J. Koeller, C. D. Spilling, *J. Org. Chem.* **1995**, *60*, 931; A. D. I. Cruz, K. J. Koeller, N. P. Rath, C. D. Spilling, I. C. F. Vasconcelos, *Tetrahedron* **1998**, *54*, 10513.

[23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, 'Gaussian 94, Revision B.2', Gaussian, Inc., Pittsburgh, PA, 1995.

[24] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr*. **1994**, *27*, 435.
[25] D. J. Watkin, R. J. Carruthers, P. Betteridge, 'CRYSTALS', Chemical Crystallography Laboratory, Oxford, 1985.
[26] J. R. Carruthers, D. J. Watkin, *Acta Crystallogr., Sect. A* **1979**, *35*, 698.

Received May 11, 1999